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Polarization and Alignment of Nuclei*

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Four methods for nuclear polarization and alignment are discussed and compared. In particular, a general theorem regarding the leading term in the expression for nuclear polarization by hfs coupling with external field is obtained. A general method is derived for treating the computation of higher order terms in the expansions of these quantities, as well for use with complicated hamiltonians, and application is made to three cases of interest. It is shown that the higher order terms are very small, in cases of interest, compared to the leading terms.

I. INTRODUCTION

THE first suggestion that nuclei can be polarized experimentally was advanced by Simon[1] in 1939. A thermodynamic argument indicated that the direct coupling of external magnetic fields of 10^5 gauss to the nuclear spins at temperatures of 0.01°K would decrease the entropy of the nuclear spin system by 20 or 30 percent. Since that time, three alternative methods have been proposed. One is the polarization of nuclei by hyperfine coupling, with an external magnetic field polarizing the electrons, which was proposed independently by Rose[2] and Gorter[3] (hereafter referred to as R-G polarization). A second method, due to Pound,[4] utilizes the electric quadrupole splitting in crystals and results in a change in the second moment of the nuclear spins only, i.e., an alignment.

We follow the nomenclature introduced by Bleaney and use the term polarization to indicate a resulting net magnetic moment of the nuclei. Alignment will indicate a condition in which the odd nuclear moments are zero but in which the even moments depart from their values for complete spatial isotropy.

Finally, there is the recent suggestion of Bleaney[5] utilizing the anisotropic hyperfine structure, which sometimes occurs in paramagnetic ions in the solid state, to obtain an alignment. Of the four methods, the requirements with regard to field strength and temperature are most favorable experimentally for the R-G polarization. Next in order of difficulty are the Pound and Bleaney alignments, and finally the direct polarization makes the greatest demands as far as large field strengths and/or low temperatures are concerned.

Nuclear polarization, in conjunction with polarized neutron beams, can be used to determine the spin of the compound state resulting from neutron capture.[6] By simply observing whether the induced activity increases or decreases upon reversal of the neutron polarization, we can determine the compound state angular momentum from the two choices $I\pm\frac{1}{2}$ where I is the spin of the target nucleus. Alternative methods would observe the capture γ-rays or the transmission of the neutron beam. Yet another approach is to observe the deviations from isotropy of the radiations (for example, γ-rays) from polarized (or aligned) nuclei.[7] Here a knowledge of the multipolarity of the emitted radiation is required in order to obtain information on the excited level. This is the only method that can be used for aligned nuclei. Finally Simon[1] has suggested that polarized nuclei can be used in further adiabatic demagnetizations to obtain temperatures of the order of 10^{-6}°K.

It is the purpose of this paper to discuss and compare the various methods of nuclear polarization and alignment with a view to clarifying the underlying assumptions that are made in the predictions of the magnitude of the effects. In Sec. II we will derive expressions for the polarization or alignment resulting from the four methods. In addition a general result regarding the leading (and most important) term in the R-G polarization is derived. Section III will contain a method of calculation which is quite useful for complicated hamiltonians and for higher order terms.

II. LOWEST ORDER POLARIZATION AND ALIGNMENT

The complete expression for the expectation value of an observable, when we are dealing with a statistical ensemble, is obtained by use of the density matrix. This is defined in the usual fashion as

$$\rho_{ij}=\frac{1}{N}\sum_{\alpha=1}^{N} c_{j\alpha}{}^{*}c_{i\alpha}, \tag{1}$$

where $c_{k\alpha}$ represents the expansion coefficients of a given system of the ensemble, ψ_α, in terms of a basic representation u_k.

$$\psi_\alpha=\sum\nolimits_k c_{k\alpha}u_k. \tag{2}$$

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[2] M. E. Rose, Phys. Rev. **75**, 213 (1949).

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[5] B. Bleaney, Proc. Phys. Soc. (London) **A64**, 315 (1951); Phil. Mag. **42**, 441 (1951).

[6] M. E. Rose, Phys. Rev. **75**, 213 (1949).

[7] J. A. Spiers, Nature **161**, 807 (1948). As shown by H. A. Tolhoek and S. R. deGroot, Physica **17**, 81 (1951), in the case of $\beta^{\pm}$ emission an anisotropy is observed only if the β-particles are observed with a polarization-sensitive detector. This would require, for example, a scattering of the β particles before they reach the detector.

The sum in (1) is taken over all the systems of the ensemble and the expectation value of an observable O is given by

$$\langle O\rangle=\mathrm{Tr}[O\rho]/\mathrm{Tr}[\rho]. \tag{3}$$

In particular, the density matrix for a system in thermal equilibrium, at a temperature T, is given by[8]

$$\rho=\exp[-\mathcal{H}/kT], \tag{4}$$

where $\mathcal{H}$ is the complete hamiltonian of the system and where we are using a canonical ensemble.

The degree of nuclear polarization of a statistical ensemble having a hamiltonian $\mathcal{H}$ is conveniently defined as

$$f_N=\frac{\mathrm{Tr}\{I_z\exp[-\mathcal{H}/kT]\}}{I\,\mathrm{Tr}\{\exp[-\mathcal{H}/kT]\}}, \tag{5}$$

where I_z is the z-component of the nuclear spin and T is the temperature of the system. The alignment is defined as

$$\Delta=\frac{\mathrm{Tr}\{I_z^2\exp[-\mathcal{H}/kT]\}}{I^2\,\mathrm{Tr}\{\exp[-\mathcal{H}/kT]\}}-\frac{I+1}{3I}. \tag{6}$$

and represents the excess of the normalized second moment over the isotropic value represented by the second term in (6).

It will be convenient to work in the strong field representation, in which case sums over electronic and nuclear states may be done separately. We will use the notation Tr_E and Tr_N to indicate the partial sums over the electronic or nuclear states, respectively.

Let us consider the various hamiltonians that enter into the four cases of interest. Since all experiments are necessarily done at helium temperatures, or below, the available states of our spin systems are just the lowest degenerate states. In this spin manifold the typical hamiltonian for a paramagnetic salt with complete quenching is given by Abragam and Pryce[9] as

$$\mathcal{H}=\sum_i\{D_iS_i^2+g_i\beta S_iH_i+A_iS_iI_i+Q_iI_i^2\}-g\beta_N\mathbf{H}\cdot\mathbf{I}. \tag{7}$$

The first term represents the second-order splitting of the electronic spin degeneracy by the combined action of the spin-orbit coupling and other terms. The $Q_iI_i^2$ term describes the nuclear spin splitting due to the interaction of the quadrupole moment of the nucleus with the electrons and the crystalline field. We have chosen coordinates along the principle axis of the crystalline electric field. The usual range of values of the constants are $A\sim 0.10^{-2}$ cm^{-1}, $D\sim 10^{-1}-10^{-2}$ cm^{-1}; $\beta\sim 10^{-4}$ cm^{-1} gauss^{-1}, $Q\sim 10^{-3}-10^{-4}$ cm^{-1} and $\beta_N\sim 10^{-7}$ cm^{-1} gauss^{-1}. In addition to these interactions there exist various spin-spin interactions between neighboring ions which we will lump together in the general term $G(S)$ with the understanding that it is a function of the electronic spin and space coordinates only. Direct nucleus-nucleus and nucleus-neighboring ion interactions are small and may be neglected. Finally, it should be noted that the temperatures available at present for practical nuclear polarization work are those resulting from adiabatic demagnetization; *viz.*, of the order of 0.2°K. Thus we see that kT will be large compared with all terms in the hamiltonian except for the term $\beta g_iH_iS_i$ when fields of the order of 10^3 gauss are used, as is customary. Saturation effects are thus of interest only for the direct coupling between electron spin and external field.

(a) Polarization by hfs Coupling (R–G)

We can write the appropriate hamiltonian as

$$\mathcal{H}=g_i\beta S_iH_i+A_iS_iI_i+G'(S), \tag{8}$$

where we have dropped the small quadrupole and direct nuclear coupling terms in Eq. (7) and where we have combined the spin-splitting (D) term and $G(S)$ in the term $G'(S)$. We wish to evaluate the leading term of f_N in an expansion in powers of (A/kT).[10] If we expand the exponential in Eq. (5), we obtain the general term for the numerator

$$[(-1)^n/(kT)^nn!]\,\mathrm{Tr}[I_z\mathcal{H}^n]. \tag{9}$$

This expression has n terms which are linear in A, the prototype term of this set being

$$\sum_i\frac{(-1)^nA_i}{(kT)^nn!}\mathrm{Tr}[I_z\mathcal{H}_e^rI_iS_i\mathcal{H}_e^{n-r-1}]$$
$$=\frac{I(I+1)(2I+1)A_z(-1)^n}{3(kT)^nn!}\mathrm{Tr}_E[\mathcal{H}_e^rS_z\mathcal{H}_e^{n-r-1}], \tag{10}$$

since

$$\mathrm{Tr}_N[I_zI_i]=\tfrac{1}{3}I(I+1)(2I+1)\delta_{zi},$$

and where

$$\mathcal{H}_e=\sum_i g_i\beta S_iH_i+G'(S),$$

contains all the purely electronic terms. Making use of the invariance of the trace to cyclic permutations Eq. (10) becomes

$$=\frac{-I(I+1)(2I+1)A_z}{3nkT}\,\frac{(-1)^{n-1}}{(kT)^{n-1}(n-1)!}\times\mathrm{Tr}_E[S_z\mathcal{H}_e^{n-1}]. \tag{11}$$

Recombining all our terms we obtain

$$f_N=\frac{-(I+1)A_z}{3kT}\,\frac{\mathrm{Tr}_E\{S_z\exp[-\mathcal{H}_e/kT]\}}{\mathrm{Tr}_E\{\exp[-\mathcal{H}_e/kT]\}}, \tag{12}$$

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[8] See R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1948), p. 347.

[9] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[10] Since the various terms of our hamiltonian do not commute, we cannot obtain terms of higher order in (A/kT) in closed form by the method of this section. However, a simple result will still hold for the (A/kT) term.

where the result for the denominator follows from noting that the leading term is $(2I+1)\,\mathrm{Tr}_E\{\exp[-\mathcal{H}_e/kT]\}$ and that the linear term in (A/kT) vanishes. Neglecting the very small effect of the hfs coupling on the degree of electronic polarization we write for the electron polarization

$$f_e=\frac{\mathrm{Tr}_E\{S_z\exp[-\mathcal{H}_e/kT]\}}{S\,\mathrm{Tr}_E\{\exp[-\mathcal{H}_e/kT]\}},\tag{13}$$

so that $f_e=1$ corresponds to complete saturation of the electron spins. Therefore,

$$f_N=-[S(I+1)A_z/3kT]f_e,\tag{14}$$

which is the result previously communicated.[2]

The only assumption made in this derivation is that $A/kT\ll 1$. This permits the following general statement: To first order in A/kT the complete effect of all interelectronic interactions on the R-G polarization is contained in their influence on the electronic susceptibility. Since this quantity is readily measured in an experiment and is usually of order 0.8–0.9, all uncertainties due to these effects can be eliminated. In particular the requirements stated by Bleaney,[5] magnetic dilution and cooling of the salt by contact with a second paramagnetic salt, are seen to be unnecessary. Experiments at this laboratory[11] have amply demonstrated that low temperatures and large electronic polarizations are obtained at quite small magnetic fields. The influence of dipole-dipole coupling on f_e has been thoroughly discussed by Van Vleck.[12]

(b) Alignment by Quadrupole Coupling (Pound)

No external field is necessary here. In fact there is no necessity for the use of a paramagnetic salt. For simplicity let us assume that we have a crystalline field of tetragonal symmetry. Under these circumstances the appropriate hamiltonian is simply

$$\mathcal{H}=Q[3I_z^2-I(I+1)],\tag{15}$$

where $Q=eq\lambda/[4I(2I-1)]$ and q is the nuclear quadrupole moment, λ is the second derivative of V (the intercrystalline field) at the nucleus, and z is the axis of symmetry of the field. Then,

$$\begin{aligned}\Delta&=-\frac{Q}{I^2kT}\left\{\frac{3}{2I+1}\mathrm{Tr}[I_z^4]-\frac{I^2(I+1)^2}{3}\right\}\\&=-\frac{Q(I+1)}{5IkT}\left[\frac{4}{3}I(I+1)-1\right],\end{aligned}\tag{16}$$

where the result follows immediately from an expansion of the exponential, noting that

$$\mathrm{Tr}_N[I_z^4]=I(I+1)(2I+1)(3I^2+3I-1)/15.$$

The inclusion of a term $A_iS_iI_i$ will not alter this result, since there is no tendency to polarize the electrons without an external field. For fields with less than tetragonal symmetry we must use the general quadrupole term given in Eq. (7). This method requires a single crystal since there is no external field to give a preferred direction in space.

(c) Alignment by Anisotropic hfs (Bleaney)

No external magnetic field is required. If we assume tetragonal symmetry and neglect the quadrupole term in (7), we have

$$\mathcal{H}=D[S_z^2-S(S+1)/3]+AI_zS_z+B(I_xS_x+I_yS_y).\tag{17}$$

The alignment cannot be calculated as simply as in our previous cases. This is due to the non-commutativity of the purely electronic and hfs terms and to the fact that the leading term is of order $(A/kT)^2$. Instead this case will be treated by the general method of the next section. For the present let us assume that $D=0$. We immediately obtain

$$\Delta=\frac{S(S+1)}{6(kT)^2I^2(2I+1)}\times\left\{\frac{A^2\,\mathrm{Tr}_N[I_z^4]+2B^2\,\mathrm{Tr}_N[I_z^2I_x^2]}{1+\dfrac{S(S+1)I(I+1)}{18(kT)^2}(A^2+2B^2)}\right\}-\tfrac{1}{3}I(I+1),$$

which becomes

$$\Delta=\frac{(A^2-B^2)(I+1)S(S+1)}{90I(kT)^2}\left[\frac{4}{3}I(I+1)-1\right],\tag{18}$$

noting that

$$\mathrm{Tr}[I_z^2I_x^2]=I(I+1)(2I+1)(2I^2+2I+1)/30.$$

This method also requires the use of a single crystal.

(d) Direct Polarization

There is no necessity to use a paramagnetic salt in this case. The only essential term in the hamiltonian is simply $g\beta_N\mathbf{H}\cdot\mathbf{I}$ and the degree of polarization is given exactly by the well-known result

$$f_N=B_I(g\beta_NH/kT),$$

where $B_I(y)$ is the brillouin function. To first order in $1/kT$ this becomes

$$f_N=g\beta_NH(I+1)/3kT,\tag{19}$$

as may be verified by use of Eq. (5).

III. HIGHER ORDER EFFECTS

The direct calculational techniques used up to this point are not very convenient when we wish to obtain the general term of an expansion of the density **matrix**

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[11] J. W. T. Dabbs and L. D. Roberts, Phys. Rev. **83**, 201 (1951).

[12] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

in terms of only one noncommuting part of the hamiltonian. The straightforward calculation leads to a result which is expressed as an infinite series for each term. This complication can be avoided by the following procedure.

We wish to expand the operator $\rho=\exp[-\mathcal{H}/kT]$, where $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$, in powers of $\mathcal{H}_1/kT$. In general $\mathcal{H}_0$ and $\mathcal{H}_1$ do not commute. Let $\tau\equiv-1/kT$. Now if the operator ϕ obeys the "equation of motion,"

$$\mathcal{H}\phi=\partial\phi/\partial\tau; \tag{20}$$

a particular solution is

$$\phi=\exp[\mathcal{H}\tau]=\rho. \tag{21}$$

Let us transform to the "interaction representation"[13] by defining an operator

$$\psi=\exp[-\mathcal{H}_0\tau]\phi, \tag{22}$$

then

$$\partial\psi/\partial\tau=\mathcal{H}_1'(\tau)\psi, \tag{23}$$

where

$$\mathcal{H}_1'(\tau)=\exp[-\mathcal{H}_0\tau]\mathcal{H}_1\exp[\mathcal{H}_0\tau];$$

note that $\psi(0)=\phi(0)=1$ and $\phi=\exp[\mathcal{H}_0\tau]\psi$. Equation (23) can be solved immediately, by an iteration technique, in powers of $\mathcal{H}_1'(\tau)$ as

$$\psi=\sum_{n=0}^{\infty}S_n, \tag{24}$$

where

$$S_n=\int_0^{\tau}\int_0^{\tau_1}\cdots\int_0^{\tau_{n-1}}\mathcal{H}_1'(\tau_1)\cdots\mathcal{H}_1'(\tau_n)d\tau_n\cdots d\tau_1,$$

$$S_0=1.$$

Using Eqs. (21) and (22) we can write the density matrix as

$$\rho=\exp[-\mathcal{H}/kT]=\exp[\mathcal{H}_0\tau]\sum_{n=0}^{\infty}S_n. \tag{25}$$

Thus we have obtained the expansion in powers of $\mathcal{H}_1$. We apply this method to three cases.

(a) Second-Order Term in R–G Polarization

For simplicity we take $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$ with

$$\mathcal{H}_0=g\beta\mathbf{S}\cdot\mathbf{H}\equiv\alpha S_z,\quad \mathcal{H}_1=A\mathbf{I}\cdot\mathbf{S}, \tag{26}$$

where we have chosen the z-axis along the direction of the external field and set $\alpha=g\beta H$. We make the usual definitions:

$$S_+=(S_x+iS_y)/\sqrt{2},\quad S_-=(S_x-iS_y)/\sqrt{2},\quad S_0=S_z.$$

Then

$$\begin{aligned}\mathcal{H}_1'(\tau)&=\exp[-\alpha S_0\tau]A(\mathbf{I}\cdot\mathbf{S})\exp[\alpha S_0\tau]\\&=AI^m\exp[-\alpha S_0\tau]S_m\exp[\alpha S_0\tau],\end{aligned}$$

where m takes on the values $(+, 0, -)$, and $Y^m=Y_{-m}$. By use of the commutation rules

$$S_0S_+=S_+(S_0+1),\quad S_0S_-=S_-(S_0-1),$$

we find

$$\mathcal{H}_1'(\tau)=AI^mS_m\exp[-\alpha m\tau]. \tag{27}$$

Then to first order in (A/kT) the density matrix is

$$\rho=\exp[\alpha S_0\tau]+AI^m\exp[\alpha S_0\tau]S_m\int_0^{\tau}\exp[-m\alpha\tau_1]d\tau_1.$$

Taking the trace of the electronic states we have

$$\mathrm{Tr}_E[\rho]=Z-(AI_z/kT)\,\mathrm{Tr}_E\{S_0\exp[\alpha S_0\tau]\},$$

where

$$Z=\mathrm{Tr}_E\{\exp[\alpha S_0\tau]\},$$

and by use of Eq. (5) we obtain the previous result of Eq. (14).

The second order term is

$$\rho_2=A^2I^mI^n\exp[\alpha S_0\tau]S_mS_n\times\int_0^{\tau}\exp[-m\alpha\tau_1]\int_0^{\tau_1}\exp[-n\alpha\tau_2]d\tau_2d\tau_1.$$

Only the terms S_+S_-, S_-S_+, and S_0S_0 will contribute to a trace over the electronic states. The integrals are readily evaluated

$$\begin{aligned}I(+,-)&=\int_0^{\tau}\exp[-\alpha\tau_1]\int_0^{\tau_1}\exp[\alpha\tau_2]d\tau_2d\tau_1\\&=(\alpha\tau+\exp[-\alpha\tau]-1)/\alpha^2,\end{aligned}$$

$$I(-,+)=(-\alpha\tau+\exp[\alpha\tau]-1)/\alpha^2,$$

$$I(0,0)=\tfrac{1}{2}\tau^2.$$

The diagonal elements of S_mS_n are given by use of

$$\begin{aligned}S_+S_-&=\tfrac{1}{2}[\mathbf{S}^2-S_z^2-S_z],\\S_-S_+&=\tfrac{1}{2}[\mathbf{S}^2-S_z^2+S_z],\\S_0S_0&=S_z^2.\end{aligned}$$

Summing over electronic states we have

$$\rho_2=(A/kT)^2Z(a_0+a_1I_z+a_2I_z^2)/\theta^2, \tag{28}$$

where

$$\begin{aligned}a_0&=-\tfrac{1}{2}I(I+1)M_1\theta,\\a_1&=M_1[1-(\theta/2)\coth(\theta/2)],\\a_2&=\tfrac{1}{2}\theta^2S(S+1)+\tfrac{1}{2}\theta M_1[1+\theta\coth(\theta/2)],\end{aligned}$$

and the first moment of the electronic spins is given by

$$M_1\equiv\tfrac{1}{2}[\coth(\theta/2)]-(S+\tfrac{1}{2})\coth(S+\tfrac{1}{2})\theta,$$

noting that

$$Z=[\sinh(S+\tfrac{1}{2})\theta]/\sinh(\theta/2),$$

with

$$\theta=g\beta H/kT.$$

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[13] The use of the interaction representation is a convenient and familiar device in quantum electrodynamics. For the definition and use of the interaction representation see, e.g., J. Schwinger, Phys. Rev. 74, 1448 (1948).

These results can be inserted in Eq. (5) to obtain the next correction to f_N, which is

$$\frac{1}{3}\left(\frac{A}{kT}\right)^2(I+1)\frac{a_1}{\theta^2} =\frac{1}{3}\left(\frac{A}{kT}\right)^2(I+1)Sf_e\left[\frac{1-(\theta/2)\coth(\theta/2)}{\theta^2}\right]. \quad (29)$$

The function in the brackets has the maximum absolute value $+\frac{1}{12}$ and thus the entire second term represents a correction of less than one percent when $T=0.2$°K and $A=0.01\ \mathrm{cm}^{-1}$.

(b) Bleaney Alignment Including the Electronic (D) Term

Here $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$ with

$$\mathcal{H}_0=D[S_z^2-\tfrac{1}{3}S(S+1)],$$
$$\mathcal{H}_1=AI_zS_z+B(I_xS_x+I_yS_y).$$

This calculation follows along similar lines. In general,

$$S_m(\tau)=S_m\exp[-Dm(2S_0+m)\tau], \quad (30)$$

and we find that the term in $(1/kT)^2$ (after taking the electronic trace) is

$$\rho_2=\tfrac{1}{2}(A/kT)^2I_z^2M_2Z +\tfrac{1}{2}(B/kT)^2[I(I+1)-I_z^2]G(\tau), \quad (31)$$

where

$$G(\tau)=\mathrm{Tr}_E\{\exp[\mathcal{H}_0\tau][S(S+1)-S_z^2-S_z]F(\tau,S_z)\},$$

$$F(\tau,S_z)=\frac{\exp[D(2S_z+1)\tau]-1-D(2S_z+1)\tau}{D^2(2S_z+1)^2\tau^2},$$

$$Z=\mathrm{Tr}_E\{\exp[\mathcal{H}_0\tau]\},$$

and M_2 is the second moment of the electronic spins. We can evaluate the traces by expanding in powers of (D/kT). The zero order term reduces to our previous result of Eq. (18). The linear term in (D/kT) becomes

$$\rho_2'=\frac{D\tau S(S+1)(2S+1)}{60(kT)^2}\left[\frac{4}{3}S(S+1)-1\right] \times\{2A^2I_z^2-B^2[I(I+1)-I_z^2]\},$$

and this is easily shown to lead to the following correction term to the Bleaney alignment:

$$\Delta'=\frac{-D[2A^2+B^2]}{900(kT)^3}\frac{(I+1)}{I}S(S+1) \times\left[\frac{4}{3}I(I+1)-1\right]\left[\frac{4}{3}S(S+1)-1\right]. \quad (32)$$

At temperatures of 0.1°K this term is of the same order as the leading term which means that the influence of the electronic splitting must be carefully investigated for a given experiment and several terms taken in the expansion. Alternatively, one can choose an ion with $S=\frac{1}{2}$ and then the D term reduces to a constant factor in the hamiltonian and has no effect, as may also be seen by the form of our result.

(c) Spin-Spin Coupling of Two Ions

The general result stated in Sec. II showed that to first order in A/kT the spin-spin coupling between ions only affected f_N by altering the value of f_e. It is of interest to inquire as to the effect of this coupling on the next higher term $(A/kT)^2$. To investigate this we assume the model of a system composed of two ions coupled together by spin-spin coupling. If λ represents the coefficient of the spin-spin coupling, we can expand the $(A/kT)^2$ term in powers of (λ/kT). The zero order term is simply part (a) of this section. The first term of interest is of order $A^2\lambda/(kT)^3$. We take $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$ with

$$\begin{aligned}\mathcal{H}_0&=g\beta\mathbf{H}\cdot(\mathbf{S}_1+\mathbf{S}_2)+\lambda\mathbf{S}_1\cdot\mathbf{S}_2,\\ \mathcal{H}_1&=A\mathbf{I}_1\cdot\mathbf{S}_1+A\mathbf{I}_2\cdot\mathbf{S}_2,\end{aligned} \quad (33)$$

where the subscripts refer to a particular ion. Since we have expanded in powers of λ, the new $\mathcal{H}_0$ is just the same as in part (a). Carrying through a similar analysis we find

$$\rho_2'=-[A^2\lambda M_1Z/2(kT)^3](a_0+a_1I_z+a_2I_z^2), \quad (34)$$

where

$$a_0=-[2I(I+1)/\theta^3]\{4M_1[1-(\theta/2)\coth(\theta/2)] +M_1\theta[1+\theta\coth(\theta/2)]+S(S+1)\theta^2\},$$

$$a_1=(M_1/\theta^2)[\theta-3\coth^2(\theta/2)+6\coth(\theta/2)] +[4S(S+1)/\theta^2][1-(\theta/2)\coth(\theta/2)],$$

$$a_2=-[a_0/I(I+1)]-2S(S+1)\coth(\theta/2) -M_1[2S(S+1)-1+3\coth^2(\theta/2)],$$

and M_1, θ, and z are the same as in case (a). The correction term to the R-G polarization is then

$$\begin{aligned}f_N'&=-[A^2\lambda/6(kT)^3]M_1(I+1)a_1\\ &=-\tfrac{1}{6}(A/kT)^2(\lambda/kT)S(I+1)f_ea_1.\end{aligned} \quad (35)$$

The term a_1 is well-behaved and has a maximum absolute value of about $+S(S+1)/3$. Thus this term is still small compared to the linear term in A/kT for $A\sim0.01$ cm^{-1}, $T\sim0.2$ °K, $\lambda/kT\sim0.1$.

These three cases illustrate the wide applicability of the method.